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Compressed CO₂ mediated synthesis of bifunctional periodic mesoporous organosilicas with tunable porosity†

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A facile and green method is proposed for the fabrication of bifunctional periodic mesoporous organosilicas (PMOs) using compressed CO₂.

Periodic mesoporous organosilicas (PMOs) are a class of hybrid inorganic-organic materials, comprising of siloxane units bridged by organic groups in an ordered mesoporous network.¹⁻⁴ In general these materials are synthesized by combining controlled hydrolysis and condensation of bridged organosilica precursors through a surfactant templated approach, whereby the supramolecular array of a surfactant in solution is entrapped by co-condensation of siloxane domains covalently linked with organic functional groups. The first synthesis of PMOs with aromatic bridges was reported by Yoshina-Ishii et al.,² where 1,4-bis(triethoxysilyl) benzene (BTEB) and 2,5-bis(triethoxysilyl)thiophene (BTET) were used as precursors with cetyltrimethylammonium bromide (CTAB) as the structure-directing agents (SDA). Above studies have generated great stimulus in the synthesis of a range of PMOs with organic functionalities incorporated into the silica pore walls. Significantly, due to tunable pore size distribution, integrated organic moieties present in the pore walls, high surface area and mesostructural ordering, PMOs find numerous applications in the field of host-guest chemistry, catalysis, adsorption, drug delivery, light harvesting etc.⁵⁻¹⁰ Recently, the multifunctional PMOs containing more than one bridging group have been synthesized using triblock copolymers nonionic surfactants, C₁₈H₃₇(EO)₁₀-OH (Brij76)¹¹⁻¹³ and EO₂₀PO₇₀EO₂₀ (P123)¹³⁻¹⁵. The introduction of multifunctional bridging groups allows finely

tune surface properties of PMOs to achieve the desired functionality and selectivity.

Acidic pH conditions are generally required when employing the PEO-PPO-PEO triblock copolymer as SDA.^{16, 17} Furthermore, to improve the porous order of these materials structured by triblock copolymers, inorganic salts such as NaCl and organic additives have been used to tailor the pore size of PMOs.^{18,19} However, the use of an additive brings about extra cost and additional parameters to be monitored. Moreover, salts are known to remain incorporated into the silica framework, that can have deleterious effects on hydrothermal stability.²⁰ Given the limitations posed by chemical additives and salts, new methodologies for the fabrication of PMOs with tunable porous architectures are highly desirable.

Supercritical or compressed CO₂ has received much interest in recent years because it is readily available, inexpensive, nontoxic, and nonflammable. Compressed CO₂ has been used in different fields, including extraction and fractionation,²¹⁻²³ chemical reactions,²⁴⁻²⁶ material science,²⁷⁻²⁹ and microelectronics^{30, 31}. CO₂ has been found to be particularly versatile in tuning the properties of a variety of surfactant assemblies.³² In light of these applications, we have employed compressed CO₂ for first time to synthesize bifunctional periodic mesoporous organosilicas containing thiophene and benzene bridging groups. Introduction of bifunctional or multifunctional bridging groups allows one to tailor the surface properties of PMOs to achieve the diverse applications with desired selectivity.³³ For instance, PMOs with benzene functionalities can act as ligand channels for metal complexes.³⁴ Whereas, thiophene functionalities have been exploited in the electrochemical applications.^{34,35} Clearly, inclusion of benzene as well as thiophene functional groups within the pore walls may allow us to construct bifunctional PMOs with novel properties. We show that by varying the pressure of CO₂, bifunctional PMO materials comprising worm-like porous network with tuneable pore size can be routinely prepared (Scheme 1). The method is greener, as it eludes the use of mineral acids, salts and organic additives. The compressed CO₂

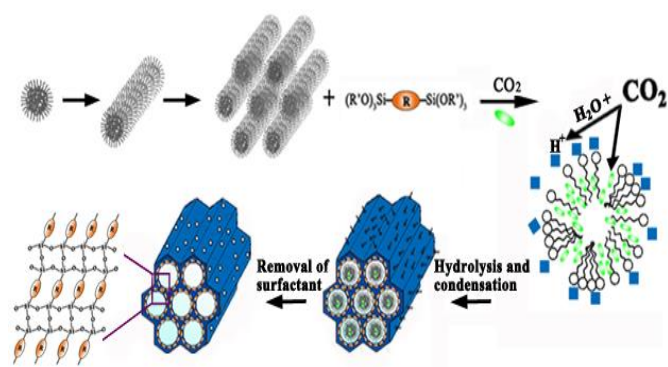
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acts as physiochemical additive and a reagent to produce acid catalyst in the sol-gel reaction and can be released completely after depressurization and easily reused to simplify the post separation processes in applications.



Scheme 1: Schematic illustration of synthesis of the bifunctional PMOs using P123 as SDA and BTEB/BTET as the organosilica precursors in presence of compressed CO₂.

In a typical synthesis, premixed solution of BTET and BTEB (Molar ratio 5:5) was added dropwise to the aqueous solution of P123 (0.088 mmol) with continuous stirring. The resulting mixture then loaded into a stainless steel autoclave and CO₂ was charged into the autoclave until a suitable pressure was reached. A magnetic stirrer in the autoclave was employed to accelerate the mixing of CO₂ and the solutions. The autoclave was kept for 24 h at 40 °C under vigorous stirring. Subsequently, the temperature of autoclave was increased to 100 °C for 24 h in an additional hydrothermal treatment step. During the processing, the pressure of the autoclave was kept constant. Finally, after depressurization, the obtained precipitate was dried and removed the surfactant by a mixture of ethanol-HCl using a Soxhlet apparatus.

A representative SEM image of the as synthesized PMOs prepared at 2.90 to 5.90 MPa showed aggregated crystal-like platelets with some connected sphere-like macrostructures (Figure S1). Transmission electron microscopy (TEM) was also employed to investigate the microstructural features of the solvent extracted PMOs. It was noted that the CO₂ pressures had significant effect on the pore morphology and structure of the as-synthesized PMOs. For instance, at the CO₂ pressures of 2.90 and 3.90 MPa, the TEM revealed disordered and poorly ordered worm-like porous structures respectively (Figure 1a and 1b). However, the samples prepared at the pressure values of 4.40 MPa showed presence of well-ordered worm-like pores with diameter of ca.2.85 nm. Significantly, at the elevated pressures of 4.90, 5.40 and 5.90 MPa the samples retained worm-like porous network with pore size 4.16 nm, 4.57 nm and 4.02 nm respectively (Figure 1c-f). The bulk structure of solvent extracted PMOs was characterized by small angle X-ray scattering (SAXS). The SAXS diffractograms of the bifunctional PMOs prepared at the pressures of 4.40, 4.90, 5.40 and 5.90 MPa are shown in Figure 2. In each case, samples revealed a typical sharp reflection in the low-angle region consistent with

the presence of mesoporous structure.

N₂ adsorption-desorption isotherms and the corresponding BJH pore size distributions of the extracted mesoporous materials are shown in Figure 3. The surface area, pore volume, and pore diameter of the samples are presented in Table 1. The PMOs materials, prepared with compressed CO₂ at 3.90 MPa, did not reveal a type IV isotherm with a pronounced capillary condensation loop. The isotherm profile and the pore size distributions were typical of disordered materials. A type-IV isotherm pattern with an H1 hysteresis loop is observed when the CO₂ pressure was increased to 4.40 MPa, which suggests that the material possess a mesoporous structure.

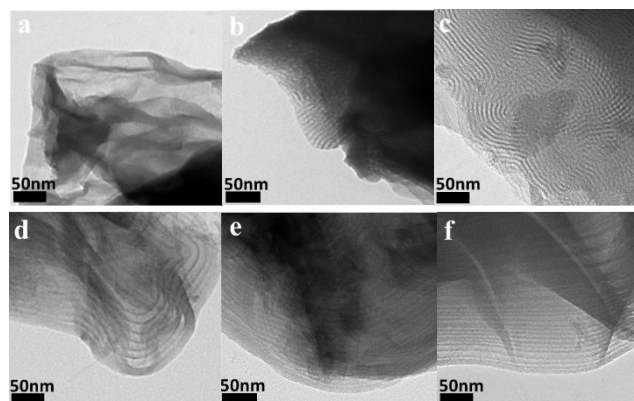


Fig. 1 TEM images of the bifunctional PMOs synthesized with P123 as SDA and BTEB/BTET as the organosilica precursors with the CO₂ pressure of (a) 2.90, (b) 3.90, (c) 4.40, (d) 4.90, (e) 5.40, and (f) 5.90 MPa.

The pore size distribution indicates the existence of mesopores with an average size of 3.2 nm according to the BJH formula. The pore volume and BET-specific surface area was calculated to be 0.21 cm³g⁻¹ and 710 m²g⁻¹ respectively. Interestingly, as the CO₂ pressures were increased the sample showed increase in the pore size and decrease in the surface area. For instance, when the pressure rose to 4.90 MPa, the pore size and pore volume also increased to 5.9 nm and 0.53 cm³g⁻¹, respectively, but the BET-specific surface area decreased to 620 m²g⁻¹. Similar trend was observed for PMOs prepared at the pressure 5.40 MPa.

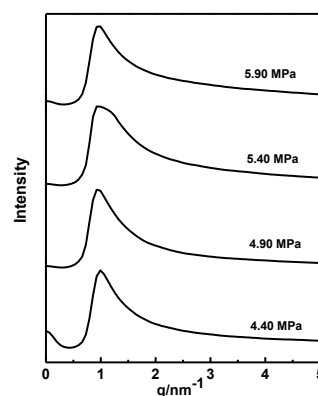


Fig. 2 SAXS patterns of the bifunctional PMOs synthesized at various compressed CO₂ pressures.

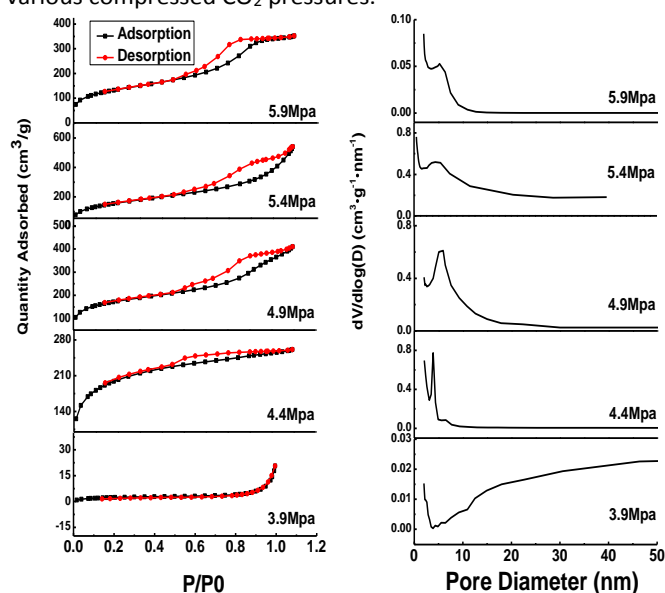


Fig. 3 Nitrogen adsorption–desorption isotherms and pore size distributions of the bifunctional PMOs with change in CO₂ pressures.

In contrast, at 5.90 MPa the samples did not retain the similar tendency suggesting that the pore size and pore volume of PMOs does not decrease monotonically with increasing pressure, but can be altered by the pressure of compressed CO₂. The ²⁹Si MAS NMR spectra for the bifunctional PMO materials are shown in Figure S2. Almost no difference was noticed in the signal intensity ratio for the PMOs prepared under different pressures, indicating that gas pressures had no effect on the composition of PMOs.

The experimental and simulated Tn signals are shown in Figure S2 and S3 respectively. The presence of both thiophene-bridged and benzene-bridged Tn species in the sample gives a convincing evidence for the incorporation of BTET and BTB

Table 1. Nitrogen physisorption data of the bifunctional PMO materials synthesized with P123 as SDA with different CO₂ pressures.

Pressure (MPa)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
3.90	9	0.03	-
4.40	710	0.21	3.2
4.90	620	0.53	5.9
5.40	586	0.82	6.5
5.90	489	0.54	5.2

into the PMO wall. Moreover they are in good agreement with the molar ratios of the corresponding organosilica precursors in the initial reaction mixtures (Table S1). The solid-state ¹³C CP MAS NMR spectra for bifunctional PMOs revealed broad peaks at 133.3 and 137.3 ppm corresponding to aryl carbons and carbons associated with the thiophene ring respectively. (Figure S4).

It is well known that CO₂ can dissolve in water and can be ionized partially ($\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$), reducing the pH.³⁶ UV-Vis spectroscopy can be used to study the pH values of the bulk water of micelles using Bromophenol Blue (BPB) as a pH indicator.^{36, 37} We employed this spectrometric method to determine the bulk change in pH of P123 micelles solutions treated with compressed CO₂ pressure conditions (Figure S5). As shown in Figure 4, it is clear that the pH value of the bulk solution decreased monotonically with the increasing pressure, indicating the acidity of the solution increases with the increasing pressure. This indicates that the pH change caused by the CO₂ mediated acidification of water can be used as a catalyst to promote the hydrolysis of the organosilica precursors. On the basis of the experimental results, a possible mechanism for the formation of PMOs with compressed CO₂ is proposed. The order and morphology of the obtained PMOs is strongly dependent on the hydrolysis and condensation kinetics of the organosilica precursors.³⁸ We note that the pH value decreases sharply below 3.90 MPa followed by steady decline in pH values with increase in the pressure. This trend clearly indicate that at pressure 3.90 MPa, the pH of the reaction mixture is not sufficient to drive the hydrolysis and condensation of the silica precursors which causes the formation of disordered PMOs. Whereas acidic pH conditions facilitated by increased gas pressures facilitate and accelerate the hydrolysis reactions.^{28, 29} As a result, the PMOs prepared at 4.40 MPa and above exhibited well-defined worm-like mesoporous structures. Significantly, pore size data analysis obtained from TEM micrographs and Nitrogen gas adsorption-desorption isotherms revealed increase in the pore diameter and pore wall thickness with increase in CO₂ pressure. For instance, at pressures 4.40 MPa, the samples revealed well-ordered mesoporous structure with average pore diameter of 3.2 nm with BET surface area of 710 m²g⁻¹. Interestingly, we note that CO₂ pressures can be utilized to tune the pore size of the PMOs. The experiments conducted at pressures 4.90 and above showed the pore size of the PMOs obtained at higher pressures was nearly doubled. This could be attributed to the increased dissolution of CO₂ that facilitates penetration of the gas molecules in the hydrocarbon-chain region of the P123 micelles.^{25, 30} As a consequence, change in the volume of block-co-polymer micelles decreases the curvature of the interface film and packing parameter becomes larger. Moreover, lower pH values obtained at higher CO₂ pressure enhances the rate of sol-gel reaction, which further contribute towards the faster condensation of hydrolyzed oligomeric species of organosiloxanes. Taken together, these conditions contribute towards the increased pore diameter and wall thickness, which inevitably lowered the average surface area of the corresponding PMOs.

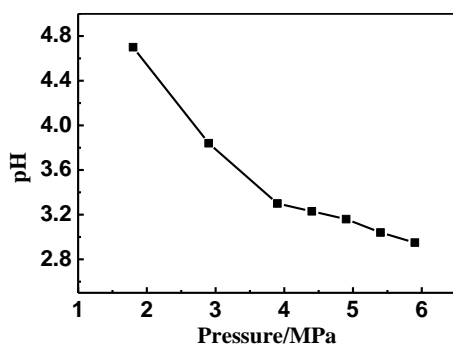


Fig. 4 pH values of the P123 solution in equilibrium as a function of pressures of compressed CO₂.

In summary, bifunctional aromatic PMOs containing thiophene and benzene bridging groups have been synthesized by employing compressed CO₂ with the triblock copolymer P123 as SDA and BTET/BTEB as organosilica precursors. We demonstrate a dual functionality of the compressed CO₂ as an acid catalyst and its ability to swell P123 micelles under higher pressures that enable us to produce bifunctional PMOs with worm-like pores with tunable size in the range of 3.2 to 6.5 nm. We envisage that this facile and green method of compressed CO₂ induced synthesis of PMOs is not limited to P123 type SDAs and can be readily extended to other surfactant assemblies. In light of above results, the use of compressed CO₂ should offer unique opportunity to synthesize a range of bifunctional, trifunctional and hybrid PMOs with desired bridged chemical functionalities for applications in sensing, controlled release and catalysis.

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